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NITROGEN REMOVAL TODAY

J. F. Kreissl

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Sanitary Engineering Institute
University of Wisconsin
Madison, Wisconsin

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Advanced Waste Treatment Research Laboratory
Environmental Protection Agency, Water Quality Office
Cincinnati, Ohio 45226

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ABSTRACT

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A review of nitrogen removal techniques is presented. The most advanced methods are stressed with presentation of available operational, economic, and theoretical factors. Other methods are cited without detail. Nitrogen removal is put into context with other treatment requirements.

NITROGEN REMOVAL TODAY*

J. F. Kreissl**

Of the three most discussed nutrients, carbon, phosphorus, and nitrogen, the latter has been the one of least concern. The recent International Joint Commission report[1] on eutrophication concentrated on phosphorus removal rather than nitrogen removal because:

1. Phosphorus contributions to Lake Erie from municipal and industrial wastes constitute 70% of the total contribution as opposed to 30 to 40% for nitrogen;
2. Efficient and reasonably-priced phosphorus removal methods are available, while nitrogen removal technology is less advanced;
3. Nitrogen sources are less controllable:
   a. greater phosphorus retention in soils,
   b. less phosphorus release from bottom sediments,
   c. significant direct contributions of nitrogen by precipitation,
   d. nitrogen-fixation ability of numerous organisms.

Despite such information there is a definite need to develop a nitrogen removal technology. Areas such as upper San Francisco Bay,

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Lake Tahoe, and Potomac Estuary as well as some states have nitrogen removal requirements. Also, nitrogen can be the limiting nutrient in water bodies where extremely slow rates of nitrogen-fixation and nitrogen-release from sediments are found[2].

The form of nitrogen in the effluent is also important. Ammonia nitrogen can represent a large portion of the ultimate BOD exerted in the stream. According to the equation for complete nitrification,

$$2\ NH_3 + 4\ O_2 \text{ ----------> } 2\ HNO_3 + 2\ H_2O \qquad (1)$$

one mg/l of ammonia-nitrogen will exert a demand of about 4.5 mg/l of oxygen. In addition, ammonia-nitrogen interferes with chlorination due to the formation of chloramines and is toxic to fish and some other aquatic life. Some researchers have assumed that ammonia- and nitrate-nitrogen are interchangeable, while others have indicated toxic effects to certain species due to the presence of ammonia. In either case, the difference is only one of problem location due to the nitrification of the ammonia to nitrate in the stream. Although nitrate-nitrogen may appear the lesser of two evils, it also presents problems in terms of eutrophication as well as its well-known association with methemoglobinemia of infants from high concentrations in drinking water.

Roughly, domestic wastewater may be expected to contain from 15 to 40 mg/l of total nitrogen. Although the distribution of this total between organic, ammonia, nitrite, and nitrate forms is highly

variable dependent upon a number of factors, the ammonia and organic forms generally predominate. In passage through conventional waste treatment facilities change in the total nitrogen concentration is generally noted. Reductions are quoted in a range of 15 to 60% depending on process design and operation for activated sludge plants[3,4]. The higher values are generally associated with plants which practice nitrification. The newer physical-chemical systems consisting of coagulation, sedimentation, filtration, and carbon adsorption generally remove organic nitrogen with no significant change in the ammonia concentration.

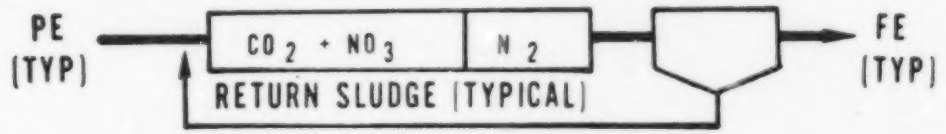
A number of nitrogen removal schemes have been tested. These include biological nitrification and denitrification, ammonia stripping, ion exchange, breakpoint chlorination, and non-specific demineralization systems. No major installations of these techniques are presently generating data for evaluation of their applicability. The South Lake Tahoe Public Utility District has a 3.75 MGD ammonia-stripping tower which is not presently operating due to cold weather conditions.

One of the most promising systems being demonstrated is biological nitrification-denitrification. A number of alternative ways are available for designing such a system. The nitrification-denitrification can be accomplished in one, two or three sludge systems depicted in Figure 1. The three sludge system has been successfully operated due to its simplification of process control problems. This design utilizes a first-stage unit for removing most of the organic carbon prior to the

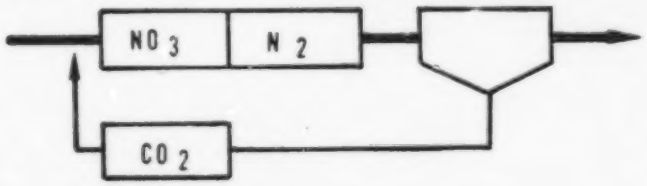
FIGURE 1
PROCESS ALTERNATIVES FOR NITRIFICATION - DENITRIFICATION

I. SINGLE SLUDGE SYSTEMS

A. EXTENDED AERATION

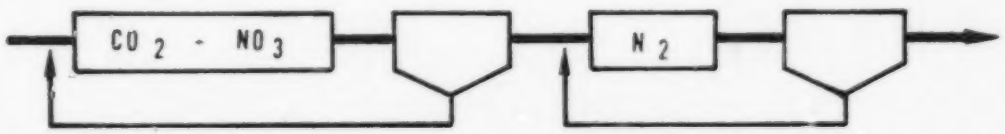


B. CONTACT STABILIZATION MODIFICATION

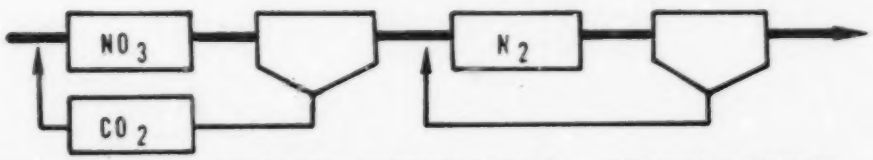


II. DUAL SLUDGE SYSTEMS

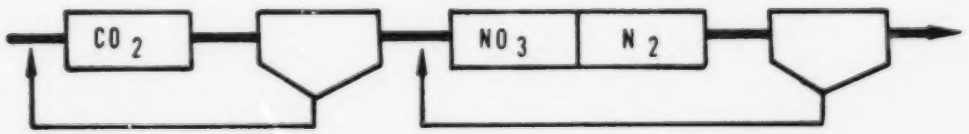
A. EXTENDED AERATION WITH ISOLATED DENITRIFICATION



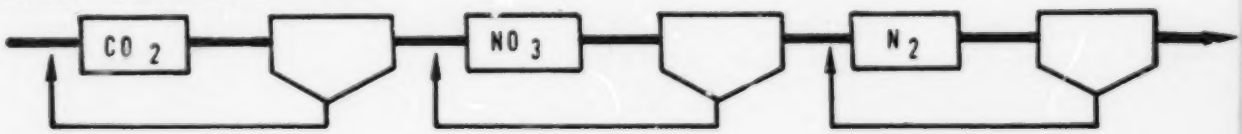
B. CONTACT STABILIZATION MODIFICATION WITH ISOLATED DENITRIFICATION



C. HIGH RATE WITH COMBINED NITRIFICATION - DENITRIFICATION



III. THREE SLUDGE SYSTEM



CODE

CO_2 CARBON REMOVAL (OXIDATION + SYNTHESIS) NO_3 NITRIFICATION N_2 - DENITRIFICATION

Reference: M. Mulbarger

second or nitrification step. This first-stage process has heretofore been high-rate activated sludge, but it is believed that a trickling filter or chemical treatment could be substituted. The first-stage unit not only accomplishes the bulk of organic removal, but also provides a buffer for the highly-sensitive nitrifiers in the second step with respect to temperature, toxic compounds, and other potential inhibitors.

Freed of the major portion of the competition in a mixed-culture, the nitrifying organisms are capable of more consistent and rapid nitrification in the second-stage reactor. Sludge production is minimal and the process should be controllable when proper cell residence time, pH, alkalinity, and other environmental factors are maintained even at waste temperatures as low as 6°C[5].

Biological denitrification can be accomplished in suspended- or fixed-growth reactors as illustrated in Figure 2. In both systems the organisms use the nitrate ion as the hydrogen acceptor in the absence of oxygen, while utilizing a readily-oxidizable carbon source. The major product of their activity is nitrogen gas. The most common source of carbon has been methanol because of low cost (25-27¢/gal) and its ability to be preferentially oxidized rather than synthesized[6]. Methanol requirements are a function of dissolved oxygen and nitrate concentrations, energy and synthesis requirements of the organisms, and the surface aeration characteristics of the tank. In general, methanol is fed at a rate of about 3 pounds per pound of nitrate-nitrogen.

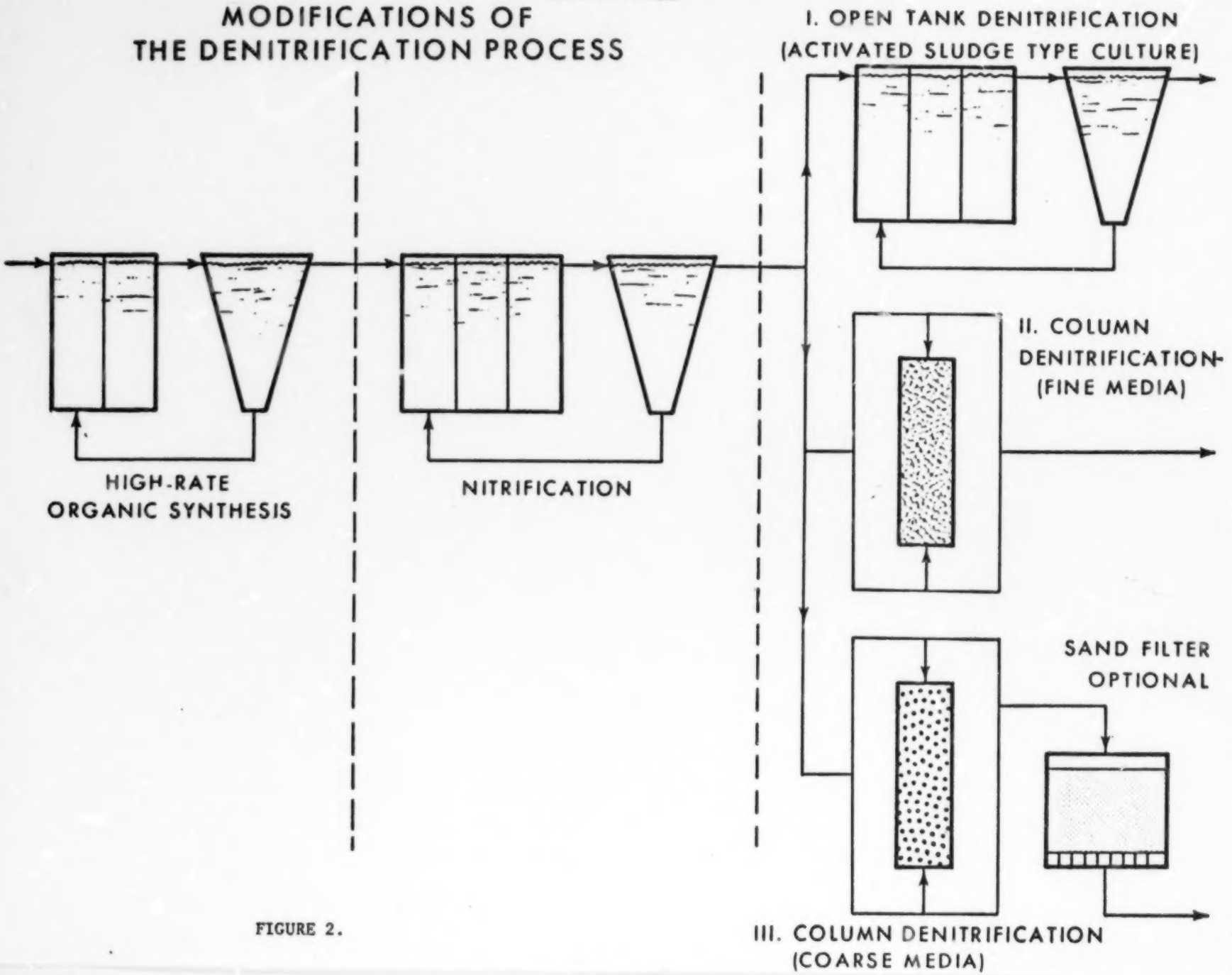

MODIFICATIONS OF
THE DENITRIFICATION PROCESS
HIGH-RATE
ORGANIC SYNTHESIS
NITRIFICATION
I. OPEN TANK DENITRIFICATION
(ACTIVATED SLUDGE TYPE CULTURE)
II. COLUMN
DENITRIFICATION
(FINE MEDIA)
SAND FILTER
OPTIONAL
III. COLUMN DENITRIFICATION
(COARSE MEDIA)

FIGURE 2.

Attempts to use waste sludges as the carbon source have been less successful due to the introduction to, and passage through the system of other nitrogen forms.

Presently, more is known about the suspended-growth systems than those with fixed growths. The results of a 185 gpd three-sludge system utilizing mineral addition for phosphorus removal in the first stage is shown in Table I[7]. These results have been successfully repeated at 0.2 MGD at waste temperatures of 12°C. In this larger installation a D.O. concentration of 0.4-0.5 mg/l was noted. The cost of adding nitrification-denitrification facilities to an existing activated sludge plant has been estimated by Smith[8] as depicted in Figure 3. To these costs must be added a final filtration cost along with the possible need for chemical addition to improve solids separation.

Although less is known about fixed-growth denitrification systems, they have been successfully used in small-scale treatment studies. Two types of fixed-growth reactors have been studied. They are fine media and coarse media systems. The coarse media system requires post-filtration in the same manner as suspended growth systems. Some work with fine media has indicated that effluent quality is not significantly impaired by sloughing of the biological growths while obtaining simultaneous clarification from filtering action. These types of studies have prompted some individuals to promote the dual-use of effluent filters as denitrifying systems as well as for clarification of the effluent. Much developmental work yet remains on this "double benefit" approach, if it is at all feasible. Backwashing problems

TABLE I. TYPICAL RESULTS – CHEMICAL PHOSPHORUS AND BIOLOGICAL DENITRIFICATION SYSTEM

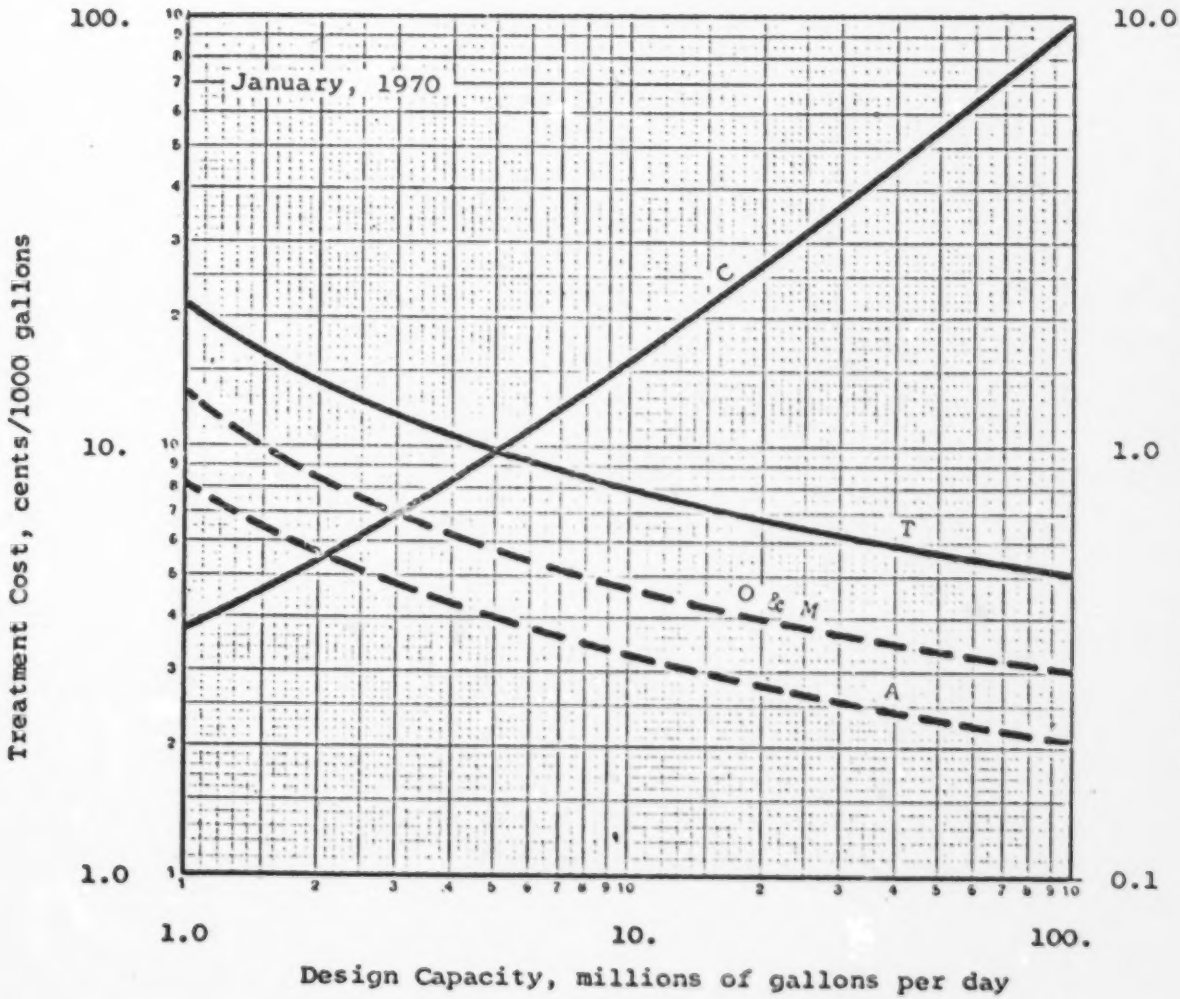
200 gpd pilot plant

PROCESS STREAM	mg/l						COMMENTS
	COD	S.S.	TKN	NO_2	NO_3	T.P.	
RAW WASTEWATER	280	125	22	—	—	16	
PRIMARY EFFLUENT	205	101	23	—	—	15	DIGESTER SUPERNATANT AND WASTE ACTIVATED SLUDGE TO PRIMARY SETTLER
HIGH-RATE EFFLUENT	50	26	8	0.5	2	3	ALUMINUM ADDED TO AERATOR
NITRIFIED EFFLUENT	30	12	1	0.0	19	2	
DENITRIFIED EFFLUENT	33	14	2	0.5	0.5	0.7	METHANOL ADDED POLISH DOSE OF ALUMINUM ADDED
OVER ALL REMOVAL	88%	89%	$\Sigma = 86\%$			95%	

FIGURE 3.

NITRIFICATION AND DENITRIFICATION IN DISPERSED GROWTH REACTORS

Capital Cost, Operating & Maintenance Cost, Debt Service
versus
Design Capacity



C = Capital Cost, millions of dollars
A = Debt Service, cents per 1000 gallons (6% and 25 yr.)
O & M = Operating and Maintenance Cost, cents per 1000 gallons
T = Total Treatment Cost, cents per 1000 gallons

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still exist. Some investigators have noted impaired denitrification immediately after backwashing while others have not[9,10]. As expected, larger media required longer contact time, while smaller media required less. Dissolved oxygen concentrations greater than one mg/l do not appear harmful to the process, but temperatures in excess of 15°C have been suggested for good results[9,10].

Common to both suspended and fixed growth systems are a number of factors:

1. Nitrogen removals of 90% have been found feasible in small-scale work;
2. Methanol/nitrate-nitrogen ratios of about 3 to 1 are generally required;
3. Nitrogen forms other than nitrate will pass through the system;
4. Nitrogen removal by these methods will drastically increase the total cost per 1000 gallons presently considered for activated sludge plants;
5. No large-scale plants are presently demonstrating these techniques.

Ammonia-stripping is the only nitrogen removal technique that has been demonstrated at a large scale. The 3.75 MGD system at Lake Tahoe has experienced difficulties in the forms of icing and scaling. The theory of the system is based on the partial pressure of ammonia in the air in contact with the waste stream containing dissolved ammonia.

If ammonia-free air is contacted with this stream the partial pressure differential offers the driving force for ammonia transfer to the gaseous phase. The theory is thoroughly treated in chemical engineering courses in mass transfer operations. As noted previously, two of the major problems associated with ammonia-stripping are freezing and scaling. Temperatures approaching 0°C increase practical air requirements for 90% ammonia removal from about 400 to about 800 cubic feet per gallon of wastewater. Freezing problems occur when wet-bulb temperatures reach 0°C[5]. Methods of heating the air have been discussed but are not considered economical for prolonged periods. Scale problems result chiefly from calcium carbonate precipitation on the tower internal appurtenances when the CO_2 in the air reacts with the unstable wastewater. The nature of this scale has varied between installations. In some it has been extremely hard, while in others it is soft and readily flushed by water jets. The nature of the scale appears to be influenced by the mode of contacting (countercurrent or crossflow), completeness of the prior precipitation, wastewater pH, and the chemical characteristics of the wastewater. One opinion suggests that countercurrent contacting with open fill towers and a lower pH ($\approx$ 10-10.5) might serve to reduce the problem[5].

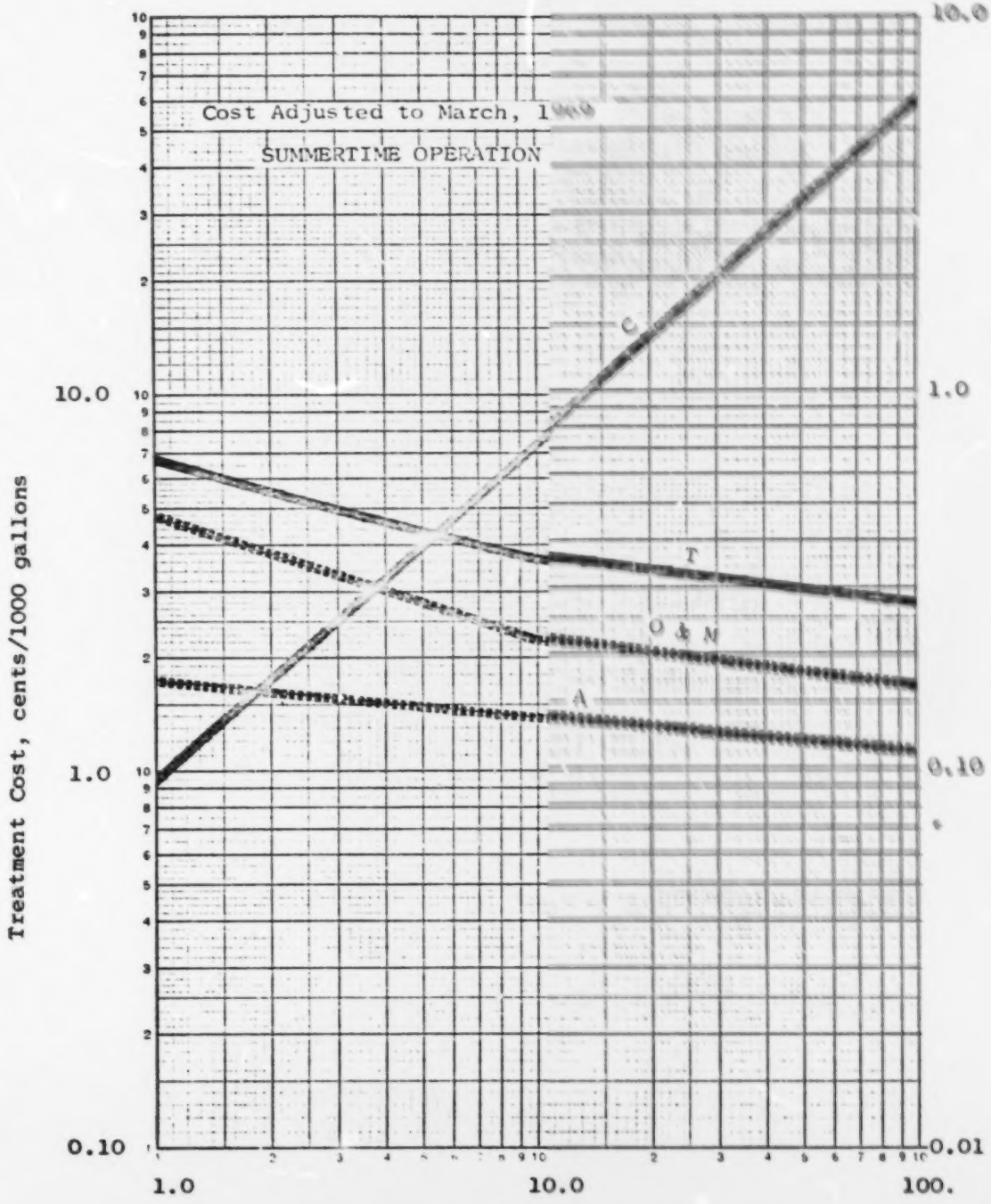
Since all cost estimates have assumed that lime precipitation of phosphorus will accompany ammonia-stripping for nitrogen removal[7], chemical and other preparatory costs are not included in these estimates. Total costs are estimated by Smith and McMichael[11] to vary from 6.5¢/1000 gal at

1 MGD to 2.8¢/1000 gal at 100 MGD for summertime conditions and 90% nitrogen removal. These costs are illustrated in Figure 4.

Some further considerations include the problems associated with ammonia-laden air emanating from the tower. The concentration of ammonia-nitrogen in the air is estimated at about 0.03 ppm which is well below the threshold of odor detection because of the enormous quantity of air required. It has been suggested that this ammonia could react with sulfur dioxide in urban areas with the possibility of resulting fogs. In any case the ammonia will be taken up by moisture in the soil, vegetation, and open water surfaces. If prevailing winds pass over large inland water bodies, the nitrogen removal effort may well be negated to a great extent[5].

Another nitrogen removal system which has been studied at small scale is selective zeolite ion exchange. A 0.1 MGD trailer-mounted demonstration plant has utilized the naturally-occurring zeolite clinoptilolite ground to 20x50 mesh for removal of ammonium ion[12]. Synthetic ion resin selectivity follows the Hofmeister or lyotropic series ($Ca > Mg > K > NH_4 > Na$), while clinoptilolite follows the order $K > NH_4 > Na > Ca > Mg$. In addition, it has a very high exchange capacity (2.0 me/g) in comparison to other natural zeolites[13]. Removals from various effluents have generally exceeded 90% through two columns in series. When a column is exhausted, it can be regenerated with limewater containing sodium chloride which hastens the regeneration rate. The high pH of the lime converts the ammonium ion to ammonia

Capital Cost, Operating & Maintenance Cost, Debt Service
vs.
Design Capacity



C = Capital Cost, millions of dollars
A = Debt Service, cents per 1000 gallons (4½ - 25 yr.)
O & M = Operating and Maintenance Cost, cents per 1000 gallons
T = Total Treatment Cost, cents per 1000 gallons

FIGURE 4.

which eventually reaches a concentration of ≈ 500 mg/l. The regenerant stream is then stripped of the ammonia and is then capable of being reused. Stripping problems in this process are similar to those of direct stripping operations. The major drawback is the increased concentration of ammonia in the effluent gas (20-30 times) which is noticeably odiferous. This operation is less susceptible to cold temperatures as heating smaller volumes of air becomes more economical. It has been noted that increased pH of the regenerant improves its performance, but also increases the rate of zeolite degradation. The exchange operation and regeneration appear to be unaffected over reasonable ranges of flow rates. Also, the process has thus far shown no susceptibility to temperature variation.

In order to circumvent the problems of air stripping, an alternative electrolytic regeneration method is being investigated whereby a neutral regenerant is used with electrolytic conversion of the ammonium ion to nitrogen gas. This method may eliminate zeolite destruction, solids accumulation, and the problems associated with stripping, but some researchers have expressed qualms concerning NCl_3 production with this system[14].

Cost estimates for a 10 MGD facility, including ion exchangers and regeneration, are 13¢/1000 gal[15]. No economics of scale have been estimated at this time, but estimates for a 300 MGD facility at Washington, D.C., are 9.7¢/1000 gal[14].

The simplest and most expedient means of removing ammonia is

breakpoint chlorination. The theoretical equations have been shown innumerable times and will not be dwelled upon here. The theoretical breakpoint equation is

$$3\ Cl_2 + 2\ NH_3 \cdots\cdots\cdots\cdots> N_2 + HCl \qquad (2)$$

In other words, 7.6 mg/l of Cl_2 are required per mg/l of NH_3-nitrogen. In practice, greater than 95% of the ammonia appears to be converted to nitrogen gas while the remaining percent appears as nitrate-nitrogen and nitrogen trichloride. Also, the required chlorine to ammonia-nitrogen ratios are about 8 to 1 if sufficient treatment has been previously imparted to the wastewater. Nitrogen trichloride production appears to be minimized with proper mixing conditions, chlorine dosing, and pH control[14].

One major drawback to breakpoint chlorination is production of an equivalent weight of hydrochloric acid. The result is the creation of high concentrations of chloride in the effluent and possible destruction of the buffer capacity with concomitant low pH's. The acidity problem can be overcome by the use of sodium hypochlorite which reacts according to the equation:

$$3\ NaOCl + 2\ NH_3 \cdots\cdots\cdots> N_2 + 3\ NaCl + 3\ H_2O \qquad (3)$$

No excess hydrochloric acid is produced when hypochlorite is used but the chemical cost is considerably higher. This increase in cost may well be offset by the relative ease and safety in handling at the plant[5].

If 20 mg/l of ammonia-nitrogen is assumed along with an 8:1

weight ratio of chlorine to ammonia-nitrogen the chemical costs of the process are about 5¢/1000 gallons. A total cost of 6.7¢/1000 gallons has been estimated for Washington's 300 MGD facility[14]. Cost reductions can be accomplished where brine or seawater is available for electrochemical production of chlorine or sodium hypochlorite.

The breakpoint chlorination method has the advantage of also providing disinfection of the effluent, which may be required by standards, anyway. It has been shown to be relatively unaffected by temperatures between 5 and 40°C when two hours of detention time was provided[14]. Some serious objections to the process have been raised concerning the unknown end products of the reaction, their toxicity to aquatic life, their public health significance, and their nuisance potential. At present, studies are being planned and conducted for the answers to these questions.

Other nitrogen removal methods have been advanced in the past. Generally, these have been dismissed or given a low priority for development. The most obvious are the general demineralization techniques such as ion exchange, reverse osmosis, electrodialysis, and distillation. None of the processes investigated thus far have favorable selectivity for ammonium or nitrate ions and may be limited to total reuse applications. Utilization of the Van Slyke reaction is being studied, but with marginal probability of feasible application.

In summary, nitrogen removal is a highly expensive and relatively untried waste treatment practice. Although biological nitrification-

denitrification appears promising, most other methods are in more preliminary stages of development. In addition, all must yet undergo the problems of scaling-up designs and operation. Other processes appear feasible if certain specific problems can be overcome. In any case, if nitrogen removal becomes a reality, waste treatment costs will undergo a significant increase.

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